



## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

\_\_\_\_\_ x  
In re Application of: :  
A. Nakajima et al. Art unit: 1755  
Serial No. 10/647,169 :  
Filed: August 21, 2003 :  
For: INK-JET IMAGE FORMING :  
METHOD :  
\_\_\_\_\_ x

DECLARATION

Honorable Commissioner of Patents  
and Trademarks  
Washington, D.C. 20231

Sir:

I, Fumio ISHII hereby declare and say as follows:

I am familiar with both the English and Japanese languages and I have compared the annexed English translation with the Japanese text of Japanese Patent Application No. 252363/2002.

To the best of my knowledge and belief, the annexed English translation is an accurate translation of the above Japanese application.

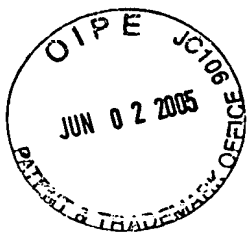
The undersigned declares further that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like

so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the U.S. Code and that such willful false statements may jeopardize the validity of the above-identified application or any patent issuing thereon.

A handwritten signature in cursive script, appearing to read "F. Ishii", is written above a horizontal line.

Fumio ISHII

Dated: This 9th day of May, 2005.



**Patent Application No. 252363/2002**

**Title of the Document:** APPLICATION FOR PATENT

**Reference Number:** DKT2484654

**Address:** The Director General of the  
Patent Office

**International  
Patent Classification:** B41J 2/01  
B41M 5/00

**Inventor(s) ;**

**Post-Office Address:** C/O Konica Corporation  
1 Sakura-machi, Hino-shi,  
Tokyo, Japan

**Name:** Yoko HIRAI

**Applicant for patent:**

**Identification Number:** 000001270

**Name:** Konica Corporation

**Representative:** Fumio IWAI

**Indication of Fee:**

**Prepayment Registration  
Number:** 012265

**Amount of Payment** 21000

**List of Documents Attached:**

**Title of Document:** Specification 1

**Title of Document:** Abstract 1

**Necessity of Proof** Required



[NAME OF DOCUMENT] SPECIFICATION

[TITLE OF THE INVENTION]

INK-JET IMAGE FORMING METHOD

[WHAT IS CLAIMED IS:]

Claim 1. An actinic radiation curable composition comprising (a) an oxetane compound in which an oxygen atom, which constitutes at least one oxetane ring in a compound which has at least two oxetane ring structures in the molecule, exhibits the highest electron density of all atoms constituting the molecule, and (b) a compound which generates a cation when exposed to actinic radiation.

Claim 2. An actinic radiation curable composition comprising (a) an oxetane compound which has at least one oxetane ring structure in the molecule, and has another oxygen atom in addition to an oxygen atom constituting an oxetane ring in the molecule, in which the electron density of an atom except for atoms which constitute said oxetane ring, is less than that of the oxygen atom constituting said oxetane ring, and (b) a compound which generates a cation when exposed to actinic radiation.

Claim 3. The actinic radiation curable composition, described in claim 1 or 2, wherein said oxetane compound has

a substituent except for a hydrogen atom at the 2-position or other position(s) of the oxetane ring.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[BACKGROUND OF THE INVENTION]

The present invention relates to an actinic radiation curable composition exhibiting excellent storage stability, which may be used to prepare inks as well as paints.

[0002]

[PRIOR ART]

Actinic radiation curable compositions are characterized in that cured compositions result in no VOC and drying energy is minimized, and are used to prepare paints, inks, coating materials, and adhesives. Specifically, cationically curable compositions have recently received attention due to desirable features such as minimum curing contraction as well as excellent close adhesion property to substrates. Known as cationically curable components are vinyl ether compounds, epoxy compounds, and oxetane compounds. Of these, oxetane compounds exhibit excellent curability and Japanese Patent Application Open to Public Inspection Nos. 7-53711, 2001-181386, and 2000-256571 disclose related techniques. However, oxetane compounds

described in those patents, when used as an actinic radiation curable composition, result in problems with poor storage stability in such a manner that when stored as a composition, physical properties vary due to an increase in viscosity.

[0003]

[PROBLEMS THEM PRESENT INVENTION INTENDS TO SOLVE]

Accordingly, an objective of the present invention is to provide a composition which exhibits excellent curability, excellent storage stability in the form of an actinic radiation curable composition, minimal variation of physical properties due to an increase in viscosity when stored in the form of a composition, high speed, and excellent storage stability.

[0004]

[MEANS TO SOLVE THE PROBLEMS]

An object of the present invention can be achieved by the following embodiments.

[0005]

1. An actinic radiation curable composition comprising (a) an oxetane compound in which an oxygen atom, which constitutes at least one oxetane ring in a compound which has at least two oxetane ring structures in the molecule, exhibits the highest electron density of all atoms

constituting the molecule, and (b) a compound which generates a cation when exposed to actinic radiation.

[0006]

2. An actinic radiation curable composition comprising (a) an oxetane compound which has at least one oxetane ring structure in the molecule, and has another oxygen atom in addition to an oxygen atom constituting an oxetane ring in the molecule, in which the electron density of an atom except for atoms which constitute said oxetane ring, is less than that of the oxygen atom constituting said oxetane ring, and (b) a compound which generates a cation when exposed to actinic radiation.

[0007]

3. The actinic radiation curable composition, described in item 1 or 2, wherein said oxetane compound has a substituent except for a hydrogen atom at the 2-position or other position(s) of the oxetane ring.

[0008]

It is possible to achieve the aforesaid objective of the present invention employing the actinic radiation curable composition described in claim 1, 2, or 3.

[0009]

The aforesaid oxetane compounds according to the present invention are comprised of at least two oxetane ring structures and include an oxetane compound in which the oxygen atom which constitutes at least one oxetane ring exhibits the highest electron density of all atoms which constitute the aforesaid oxetane ring, or an oxetane compound, having an oxygen atom other than atoms constituting an oxetane ring, in which the electron density of the atom other than atoms which constitute the aforesaid oxetane ring is lower than that of the oxygen atom which constitutes the aforesaid oxetane ring. The present invention is achieved by employing any of the aforesaid oxetane compounds. Electron density, as described herein, refers to the value calculated based on a molecular orbital calculation method, employing WinMOPAC (manufactured by Fujitsu Ltd.).

[0010]

Of those satisfying such conditions, preferably employed are an oxetane compound which has a substituent other than a hydrogen atom at the 2-position, and further an oxetane compound which has, in the molecule, at least one oxetane ring having the structure represented by General Formula (1), described below. The compound represented by



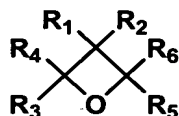
General Formula (1) is only one example and is not limited thereto.

[0011]

An oxetane compound of the present invention, represented by General Formula (1), has preferably at least one group derived from the oxetane ring in the molecule.

[0012]

General Formula (1)



[0013]

wherein,  $R_1 - R_6$  each represents a hydrogen atom or a substituent, however, at least one of the groups represented by  $R_3 - R_6$  is a substituent.

[0014]

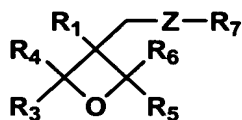
In General Formula (1),  $R_1 - R_6$  each represents a hydrogen atom, a fluorine atom or an alkyl group having 1 - 6 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group or a butyl group), a fluorinated alkyl group having 1 - 6 carbon atoms, an allyl group, an aryl group (e.g., a phenyl group, a naphthyl group, a furyl group or a thienyl group). These may further have a substituent.

[0015]

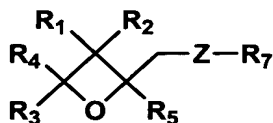
A compound having an oxetane ring in the molecule is represented by General Formulas (2) - (5) described below.

[0016]

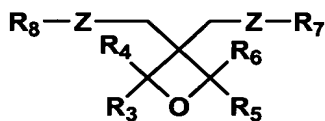
General Formula (2)



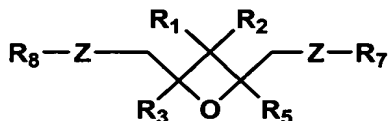
General Formula (3)



General Formula (4)



General Formula (5)



[0017]

In General Formula (2) to (5), Z represents independently an oxygen atom or a sulfur atom, or a divalent hydrocarbon group which may have an oxygen atom or a sulfur atom in the main chain.

$R_1 - R_6$  each represents a hydrogen atom, a fluorine atom or an alkyl group having 1 - 6 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group or a butyl group), an fluorinated alkyl group having 1 - 6 carbon atoms, an ally group, an aryl group, a furyl group or a thienyl group.

$R_7$  and  $R_8$  each represents an alkyl group having 1 - 6 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group or a butyl group), an alkenyl group having 1 - 6 carbon atoms (e.g., a 1-propenyl group, a 2-propenyl group, a 2-methyl-1-propenyl group, a 2-methyl-2-propenyl group, a 1-butenyl group, a 2-butenyl group, or a 3-butenyl group), an aryl group (e.g., a phenyl group, a benzyl group, a fluorobenzyl group, a methoxybenzyl group or a phenoxybenzyl group), an alkylcarbonyl group having 1 - 6 carbon atoms (e.g., a propylcarbonyl group, a butylcarbonyl group, or a pentylcarbonyl group), an alkoxycarbonyl group having 1 - 6 carbon atoms (e.g., an ethoxycarbonyl group, a propoxycarbonyl group, or a butoxycarbonyl group), an alkylcarbamoyl group having 1 - 6 carbon atoms (e.g., a propylcarbamoyl group or a butylpentylcarbamoyl group, or an

alkoxy carbamoyl group having 1 - 6 carbon atoms (e.g., an ethoxycarbamoyl group)

In General Formulas (2) and (4), at least one of  $R_3$  or  $R_4$ , or one of  $R_5$  or  $R_6$  is not a hydrogen atom.

[0018]

At least one of the groups represented by  $R_1$  to  $R_8$  or  $Z$  contains an oxygen atom, and the oxygen atom is required to have a lower electron density than a oxygen atom in a oxetane ring. The electron density is a value obtained using a molecular orbital calculation software "WinMopac".

[0019]

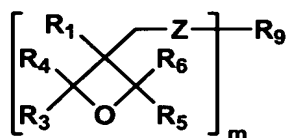
When a sulfur atom is contained in one of the groups represented by  $R_1$  to  $R_8$  or  $Z$ , the sulfur atom is also required to have a lower electron density than a oxygen atom in a oxetane ring.

[0020]

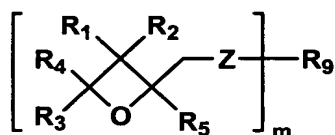
Preferable oxetane compounds having at least two oxetane groups in the molecule are represented by General Formulas (6) and (7) described below.

[0021]

General Formula (6)



General Formula (7)



[0022]

In General Formulas (6) and (7); m represents 2, 3, or 4; Z represents independently an oxygen atom or a sulfur atom, or a divalent hydrocarbon group which may have an oxygen atom or a sulfur atom in the main chain.

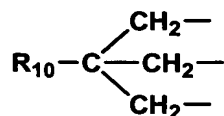
R<sub>1</sub> - R<sub>6</sub> each represents a hydrogen atom, a fluorine atom or an alkyl group having 1 - 6 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group or a butyl group), an fluorinated alkyl group having 1 - 6 carbon atoms, an allyl group, an aryl group, a furyl group.

[0023]

R<sub>9</sub> represents a straight or branched alkylene group having 1 - 12 carbon atoms. Examples are alkylene groups represented by General Formula (8) described below.

[0024]

General Formula (8)



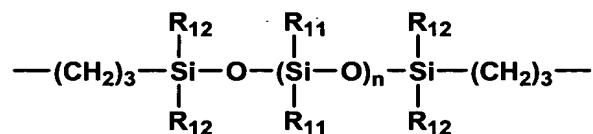
[0025]

wherein  $\text{R}_{10}$  represents a lower alkyl group (e.g., a methyl group, an ethyl group, or a propyl group).

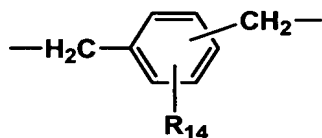
In General Formula (6) and (7),  $\text{R}_9$  represents a polyvalent group represented by General Formulas (9), (10) and (11).

[0026]

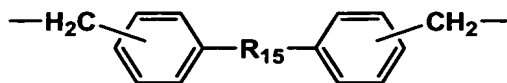
General Formula (9)



General Formula (10)



General Formula (11)



[0027]

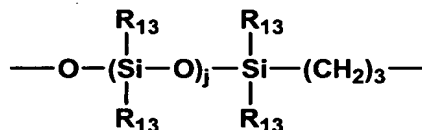
In General Formula (9)  $n$  represents 0 or an integer of 1 - 2,000,  $\text{R}_{11}$  represents an alkyl group having 1 - 10 carbon

atoms or the group represented by General Formula (12) described below.

$R_{12}$  represents an alkyl group having 1 - 10 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, a butyl group).

[0028]

General Formula (12)



[0029]

In General Formula (12),  $j$  represents 0 or an integer of 1 - 100, and  $R_{13}$  represents an alkyl group having 1 - 10 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, a butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, or a nonyl group).

[0030]

In General Formula (10),  $R_{14}$  represents a hydrogen atom, an alkyl group having 1 - 10 carbon atoms (e.g., a methyl group, an ethyl group, a propyl group, a butyl group), an alkoxy group having 1 - 10 carbon atoms (e.g. a methoxy group, an ethoxy group, a propoxy group, a butoxy group, and a pentoxy group), a halogen atom (e.g., a fluorine atom, a

chlorine atom, a bromine atom, or an iodine atom), a nitro group, a cyano group, a mercapto group, an alkoxy carbonyl group of lower alkyl number (e.g., a methyloxy carbonyl group, an ethyloxy carbonyl group, or a butyloxy carbonyl group), or a carboxyl group.

[0031]

In General Formula (11),  $R_{15}$  represents an oxygen atom, a sulfur atom,  $-NH-$ ,  $-SO-$ ,  $-SO_2-$ ,  $-CH_2-$ ,  $-C(CH_3)_2-$ , or  $-C(CF_3)_2-$ .

[0032]

In the present invention, of these compounds, useful compounds include an oxetane compound which is comprised of at least two oxetane rings in which the electron density of the oxygen atom constituting at least one oxetane ring is higher than that of atoms constituting the other molecule or an oxetane compound in which at least one of  $R_1 - R_8$  and  $Z$  is represented by an oxygen atom and the electron density of the oxygen atom constituting the oxetane ring is higher than that of atoms other than atoms constituting the oxetane ring. Namely, useful conditions of the present invention are that the electron density of atoms constituting the other portion of the molecule does not exceed that of the oxygen atom constituting the oxetane ring. Two oxetane rings are



preferably joined via an alkylene group employing it as a joint portion.

[0033]

Atoms constituting the other portion of the molecule include a carbon atom, an oxygen atom, a sulfur atom, and the like. Herein, it is necessary that based on the WinMopac calculation, the electron density of atoms other than atoms, such as an oxygen atom or a sulfur atom, constituting the oxetane ring does not exceed that of the oxygen atom in the oxetane ring.

[0034]

Compounds usable in the present invention are listed below.

[0035]

		Electron Density of Oxygen in Oxetane	Electron Density of Oxygen out of Oxetane
1		-0.245	-0.182
2		-0.301	-0.280
3		-0.281	-
4		-0.299	-0.283(methoxy)
5		-0.301 -0.296	-0.275 -0.284(methoxy)
6		-0.282 -0.281	-
7		-0.282	-0.275
8		-0.277	-
9		-0.320 -0.319	-0.290(methoxy) -0.260(methoxy)
10		-0.278 -0.277	-
Comparative		-0.275	-0.275

[0036]

While referring to publications listed below, it is possible to synthesize compounds, according to the present invention, comprised of an oxetane ring in which at least the 2-position is substituted in which the electron density of atoms other than atoms constituting the aforesaid oxetane ring does not exceed that of the oxygen atom in the oxetane ring.

[0037]

- (1) Hu Xianming, Richard M. Kellogg, *Synthesis*, 533 - 538, May (1995)
- (2) A. O. Fitton, J. Hill, D. Ejane, R. Miller, *Synth.*, 12, 1140 (1987)
- (3) Toshiro Imai and Shinya Nishida, *Can. J. Chem.* Vol. 59, 2503 - 2509 (1981)
- (4) Nobujiro Shimizu, Shintaro Yamaoka, and Yuho Tsuno, *Bull. Chem. Soc. Jpn.*, 56, 3853 - 3854 (1983)
- (5) Walter Fisher and Cyril A. Grob, *Helv. Chim. Acta.*, 61, 2336 (1987)
- (6) *Chem. Ber.* 101, 1850 (1968)
- (7) "Heterocyclic Compounds with Three- and Four-membered Rings", Part Two, Chapter IX, Interscience Publishers, John Wiley & Sons, New York (1964)

- (8) Bull. Chem. Soc. Jpn., 61, 1653 (1988)
- (9) Pure Appl. Chem., A29 (10), 915 (1992)
- (10) Pure Appl. Chem., A30 (2 & amp;3), 189 (1993)
- (11) Japanese Patent Application Open to Public Inspection  
No. 6-16804
- (12) DE 10221858
- (13) Journal; Bishoff: Chem. Ber. 28 1895; 28 29
- (14) Journal; Patemo; GCITA 9; Gazz. Chim. Ital.;  
441;1914;154
- (15) Chemical Communications 1969, 12.

The amount of compounds according to the present invention, which have an oxetane ring in which at least position 2 is substituted, in a photocurable ink is preferably 1 - 97 percent by weight, and is more preferably 30 - 95 percent by weight.

[0038]

(Use of oxetane compounds in combination with other monomers)

Further, compounds according to the present invention, which have oxetane ring(s) in which at least position 2 is substituted, may be employed individually or in combinations with two types which have different structures. Further, the aforesaid compound may be employed in combination with photopolymerizable compounds such as photopolymerizable

monomers or polymerizable monomers described below. When employed in combinations, it is preferable that a mixture is prepared so that the amount of compounds having oxetane ring(s) in the aforesaid mixture is adjusted to 10 - 98 percent by weight. Still further, it is preferable that the amount of other photopolymerizable compounds such as photopolymerizable monomers and polymerizable monomers is adjusted to 2 - 90 percent by weight.

[0039]

Employed as photopolymerizable cationic monomers may be various types of cationic polymerizable monomers known in the art. Listed, for example, are epoxy compounds, vinyl ether compounds, and oxetane compounds exemplified in Japanese Patent Application Open to Public Inspection Nos. 6-9714, 2001-31892, 2001-40068, 2001-55507, 2001-310938, 2001-310937, and 2001-220526.

[0040]

Listed as epoxy compounds are aromatic epoxides, alicyclic epoxides, and aliphatic epoxides.

[0041]

As preferable aromatic epoxides are listed, di- or poly-glycidyl ether, which is synthesized by the reaction of polyhydric phenol having at least one aromatic core or

alkylene oxide-added polyhydric phenol and epichlorohydrin, and for example, di- or poly-glycidyl ether of bisphenol A or of alkylene oxide-added bisphenol A, di- or poly-glycidyl ether of hydrogenated bisphenol A or of alkylene oxide-added hydrogenated bisphenol A, and novolak type epoxy resin. Herein, as alkylene oxide, ethylene oxide and propylene oxide are listed.

[0042]

As preferable alicyclic epoxides are listed, a cyclohexene oxide or cyclopentene oxide, which is obtained by epoxidation of the compound having cycloalkane ring such as at least one cyclohexene or cyclopentene ring by the appropriate oxidant such as hydrogen peroxide or peracid.

[0043]

As preferable aliphatic epoxides are listed, di- or poly-glycidyl ether of aliphatic polyvalent alcohol or of alkylene oxide-added aliphatic polyvalent alcohol, and as its representative example, di-glycidyl ether of alkylene glycol such as di-glycidyl ether of ethylene glycol, di-glycidyl ether of propylene glycol and glycidyl ether of 1, 6-hexane diol, poly-glycidyl ether of polyvalent alcohol such as di- or tri-glycidyl ether of glycerin or of alkylene oxide added glycerin, and di-glycidyl ether of polyalkylene glycol such

as di-glycidyl ether of polyethylene glycol or of alkylene oxide-added polyethylene glycol, and di-glycidyl ether of polypropylene glycol or of alkylene oxide-added polypropylene glycol, are listed. Herein, as alkylene oxide, ethylene oxide and propylene oxide.

[0044]

Among these epoxides, when the quick hardening ability is considered, aromatic epoxide and alicyclic epoxide are preferable, and particularly, alicyclic epoxide is preferable. In the present invention, on kind of the above epoxides may be solely used, and more than 2 kinds of them may also be used by appropriately being combined.

[0045]

Also as vinyl ether compounds preferably used in the ink of the present invention are listed: publicly known vinyl ether compounds can be used, and for example, di or tri-vinyl ether compound, such as ethylene glycol di-vinyl ether, di-ethylene glycol di-vinyl ether, tri-ethylene glycol di-vinyl ether, propylene glycol di-vinyl ether, di-propylene glycol di-vinyl ether, butane diol di-vinyl ether, hexane diol di-vinyl ether, cyclohexane di-methanol di-vinyl ether, tri-methylol propane tri-vinyl ether, or mono vinyl ether compound, such as ethyl vinyl ether, n-butyl vinyl ether,

iso-butyl vinyl ether, octadecyl vinyl ether, cyclohexyl vinyl ether, hydroxy butyl vinyl ether, 2-ethyl-hexyl vinyl ether, cyclo-hexane di-methanol mono-vinyl ether, n-propyl vinyl ether, iso-propyl vinyl ether, iso-propenyl ether-o-propylene carbonate, dodecyl vinyl ether, or di-ethylene glycol mono vinyl ether vinyl ether.

[0046]

Among these vinyl ether compounds, when the hardenability, adhesion or surface hardness is considered, di or tri-vinyl ether compound is preferable, and particularly di-vinyl ether compound is preferable. In the present invention, one kind of the above vinyl ether compounds may also be used, and more than two kinds of them may also be used by being appropriately combined.

[0047]

Listed as cyclic ethers are oxetanes such as oxetane and phenyloxetane, tetrahydrofurans such as tetrahydrofuran and 2-methyltetrahydrofuran, tetrahydropyrans such as tetrahydropyran and 3-propyltetrahydropyran, and trimethylene oxide, and s-trioxane. Listed as lactones are  $\beta$ -propiolactone,  $\gamma$ -butyrolactone,  $\delta$ -caprolactone, and  $\delta$ -valerolactone. Listed as oxazolines are oxazoline, 2-



phenyloxazoline, and 2-decyloxazoline. These monomers may be employed individually or in combination.

[0048]

Employed as maleinimide derivatives may be conventional compounds known in the art.

For example, employed may be compounds described in Japanese Patent Application Open to Public Inspection Nos. 61-250064, 62-64813, 62-79243, 6-298817, 11-124403, 11-292874, 11-302278, and 2000-264922, "Polymer Materials Science and Engineering", Volume 72, pages 470 - 472 (1995), "Polymer Preprints" Volume 37, pages 348 and 349 (1996), "Dai 4 Kai Fusion UV Gijutsu Seminar (The 4th Fusion UV Technical Seminar)" pages 43 - 77 (1996), "Polymer Letters", Volume 6, pages 883 -888 (1998), and "Dai 9 Kai Fusion UV Gijutsu Seminar (The 9th Fusion UV Technical Seminar)" pages 5 - 20 (2001).

[0049]

Further, without any special limitation, employed as compounds which copolymerize with maleinimide derivatives may be conventional compounds known in the art. For example listed may be compounds described in Japanese Patent Application Open to Public Inspection Nos. 11-124403, 11-292874, 11-302278, and 2000-264922, "Polymer Materials

Science and Engineering", Volume 72, pages 470 - 472 (1995), "Dai 4 Kai Fusion UV Gijutsu Seminar (The 4th Fusion UV Technical Seminar)" pages 43 - 77 (1996), and "Dai 9 Kai Fusion UV Gijutsu Seminar (The 9th Fusion UV Technical Seminar)" pages 5 - 20 (2001). These monomers may be employed individually or in combination.

[0050]

A cation generating agent by irradiation of an actinic ray is listed a photo-acid generating agent.

[0051]

As the photo acid generator, for example, a chemical amplification type photo resist or compound used for the light cationic polymerization is used (Organic electronics material seminar "Organic material for imaging" from Bunshin publishing house (1993), refer to page 187 - 192). Examples preferable for the present invention will be listed below.

[0052]

Firstly, aromatic onium compound  $B(C_6F_5)_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ ,  $SbF_6^-$ ,  $CF_3SO_3^-$  salt, such as diazonium, ammonium, iodonium, sulfonium, phosphonium, can be listed.

[0053]

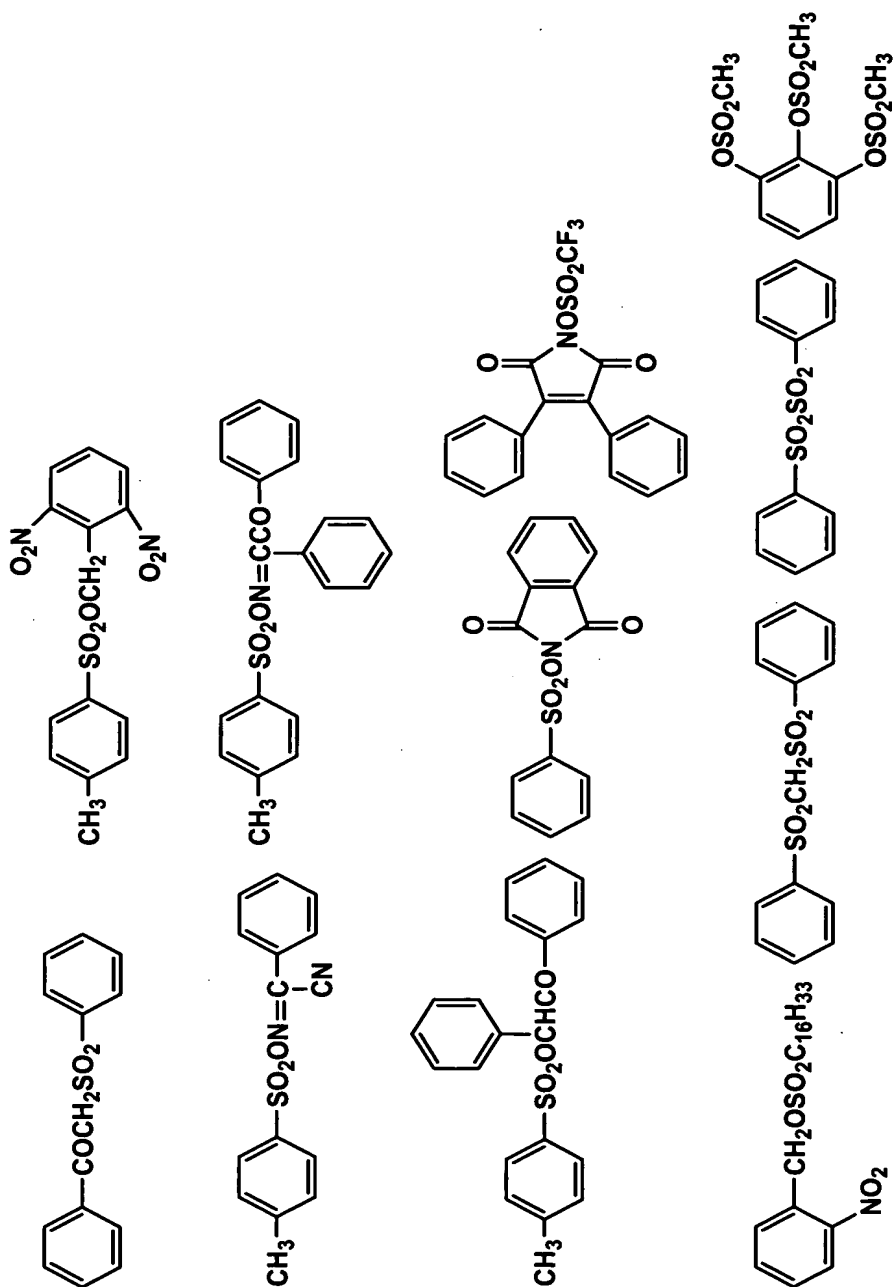
Specific examples of the onium compounds will be shown below.



[0055]

Secondly, sulfone compounds, which generate sulfonic acid, can be listed. Examples of specific compounds will be shown below.

[0056]



[0057]

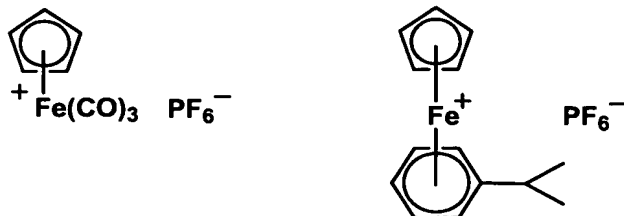
Thirdly, halogenide which generates hydrogen halide can also be used. Examples of specific compounds will be shown below.



[0059]

Fourthly, ferrite allene complex can be listed.

[0060]



[0061]

Further, the actinic radiation curable composition of the present invention is cured by exposure to actinic radiation such as ultraviolet radiation. In order to more efficiently conduct the curing reaction, it is possible to simultaneously use photosensitizers. Examples of such photosensitizers include amines such as triethanolamine, methyldiethanolamine, triisopropanolamine, methyl 4-dimethylaminobenzoate, isoamyl 4-dimethylaminobenzoate, ethyl 2-diethylaminobenzoate, n-butoxyethyl 4-dimethylaminobenzoate, and 2-ethylhexyl 4-dimethylaminobenzoate, cyanine, phthalocyanine, merocyanine, porphyrin, spiro compounds, ferrocene, fluorene, flugide, imidazole, perylene, phenazine, phenothiazine, polyene, azo compounds, diphenylmethane, triphenylmethane, polymethine acridine, coumarin, ketocoumarin, quinacridone, indigo,



styryl, pyrylium compounds, pyrromethene compounds, pyrazolotriazole compounds, benzothiazole compounds, barbituric acid derivatives, and thiobarbituric acid derivatives. Further, employed are compounds described in European Patent No. 568,993, U.S. Patent Nos. 4,508,811 and 5,227,227, and Japanese Patent Application Open to Public Inspection Nos. 2001-125255 and 11-271969. The used amount of photosensitizers is preferably in the range of 0.01 - 10.00 percent by weight in the actinic radiation curable composition.

[0062]

In order to improve various kinds of performance, it is also possible to add materials such as coloring agents (colorants), silane coupling agents, polymerization inhibitors, and leveling agents to the actinic radiation curable composition of the present invention in amounts in which original characteristics are not degraded.

[0063]

Listed as silane coupling agents are, for example,  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\gamma$ -(2-aminoethyl)aminopropyltrimethoxysilane, and  $\gamma$ -mercaptopropyltrimethoxysilane.

[0064]

Listed as polymerization inhibitors are, for example, methoquinone, methylhydroquinone, and benzoquinone. Further, listed as leveling agents are, for example, Modaflo (manufactured by Monsanto Co.) and FC-430 (manufactured by 3M Co.).

[0065]

<<Colorants>>

In order to color an active ray curable resin composition of the present invention, colorants may be added thereto. As the colorants in the present invention are, the colorants, which can be solved or dispersed in main component of the polymeric compound, can be used, however, from the viewpoint of weather fastness, the pigment is preferable.

[0066]

Examples of pigments are; a organic pigment such as a phthalocyanine type, an azo type, a quinacridone type, a dioxanedine type, a dicetopyrrolopyrrole type; and an inorganic pigment such as carbon black, titanium white, silica, mica and zinc oxide.

[0067]

As the pigment, the followings can be used.

C.I. Pigment Yellow-1, 3, 12, 13, 14, 17, 81, 83, 87, 95,  
109, 42,  
C. I. Pigment Orange-16, 36, 38,  
C. I. Pigment Red-5, 22, 38, 48:1, 48:2, 48:4, 49:1, 53:1,  
57:1, 63:1, 144, 146, 185, 101,  
C. I. Pigment Violet-19, 23,  
C. I. Pigment Blue-15:1, 15:3, 15:4, 18, 60, 27, 29,  
C. I. Pigment Green-7, 36  
C. I. Pigment White-6, 18, 21,  
C. I. Pigment Black-7.

Further, in the present invention, in order to enhance covering power of color on transparent substrates such as plastic film, it is preferable to use a white ink. Specifically, in soft package printing and label printing, it is preferable to use a white ink. However, since the ejection amount increases, from the viewpoint of the aforesaid ejection stability, and the formation of curling and wrinkling, the amount to be used is obviously limited.

[0068]

To disperse the pigment, a ball mill, sand mill, attritor, roll mill, agitator, Henschel mixer, colloid mill, ultrasonic homogenizer, Pearl mill, wet jet mill, or paint shaker may be used. Further, when the pigment is dispersed,

the dispersing agent can also be added. It is preferable that, as the dispersing agent, high polymeric dispersing agent is used. As the high polymeric dispersing agent, Solsperse series of Avecia co., is cited.

Further, as the dispersion auxiliary agent, the synergist corresponding to each kind of pigment can also be used. It is preferable that 1 - 50 parts by weight of these dispersing agent and dispersion auxiliary agent are added to 100 parts by weight of the pigment. The dispersion medium is solvent or polymeric compound, and it is preferable that the ultraviolet ray-curable ink used in the present invention comprises no-solvent, because it is reacted and hardened just after the arrival of the ink. When the solvent remains in the hardened image, the problem of deterioration of solvent resistance and VOC (Volatile Organic Compound) of the remained solvent is raised. Accordingly, it is preferable in the dispersion aptitude that the dispersion medium is not solvent, but polymeric compounds, and the monomer in which the viscosity is lowest in them, is selected.

[0069]

When the dispersion is conducted, it is preferable to configure the pigment, dispersing agent, selection of diluent for the dispersion so that average particle size of the

pigment become 0.08 - 0.5  $\mu\text{m}$ , more preferably 0.3 - 10  $\mu\text{m}$ , still more preferably, 0.3 - 3  $\mu\text{m}$ . By this particle size control, the nozzle plugging of the ink-jet head is suppressed, and the preservation stability of the ink, ink transparency and hardening sensitivity can be maintained.

[0070]

It is preferable for the colorant that the addition amount is 1 weight% to 10 weight% of the whole of the ink.

[0071]

<<Additives>>

Other than the compounds described above, it is possible to use various additives in the actinic radiation curable composition according to the present invention. For example, in order to enhance the storage stability of compositions, it is possible to add polymerization inhibitors in an amount of 2,000 - 20,000 ppm. It is preferable that an ultraviolet radiation curable ink is ejected while heated to decrease its viscosity. As a result, in order to minimize clogging of head nozzles due to thermal polymerization, it is preferable to add polymerization inhibitors. Other than these, if desired, it is possible to add surface active agents, leveling additives, matting agents, polyester based

resins, polyurethane resins, vinyl based resins, acryl based resins, rubber based resins, and wax to adjust physical properties of layers. In order to improve close adhesion properties to recording media, it is effective to add organic solvents in very minute amounts. In such cases, the aforesaid addition is effective in a range in which solvent resistance is not adversely affected and negligible VOC problems occur. The used amount is in the range of 0.1 - 5 percent and preferably in the range of 0.1 - 3 percent.

[0072]

Further, incorporated as additives to actinic radiation curable resinous compositions in the present invention may be reaction retarding agents, fillers, fluid aids, thixotropy agents, humectants, defoamers, and plasticizers. Further added may be stabilizers such as lightfastness enhancing agents, UV absorbers, antioxidants, polymerization inhibitors or corrosion inhibitors, or Si based compounds and wax. In order to adjust surface tension, if desired, incorporated may be surface active agents.

[0073]

<<Image Forming Method>>

An image forming method, employing the actinic radiation curable resinous composition according to the present invention, will now be described.

[0074]

A method which is preferred as the image forming method of the present invention is that the aforesaid actinic radiation curable resinous composition is ejected as an ink composition onto a recording material, employing an ink-jet recording system to form images, and subsequently the ink is cured while exposed to actinic radiation such as ultraviolet radiation.

[0075]

<<Total Ink Layer Thickness after Ink Impingement>>

In the present invention, the total ink layer thickness after curing, while ink comprised of the actinic radiation curable resinous composition according to the present invention, is impinged on the recording material and exposed to actinic radiation is preferably 2 - 20  $\mu\text{m}$ . In the actinic radiation curable ink-jet recording of the screen printing field, at present, the total ink layer thickness usually exceeds 20  $\mu\text{m}$ . In the soft package printing field, in which recording materials are comprised of relatively thin plastic

materials, excessive ink ejection, which results in a thick ink layer, is not preferred because problems occur in which stiffness as well as the feeling of quality of the entire printed materials varies, in addition to the aforesaid problems of curling and wrinkling of recording materials.

[0076]

Incidentally, "total ink layer thickness", as described herein, refers to the maximum value of the ink layer thickness of images formed on recording materials. The aforesaid total layer thickness is applied in the same manner, even though 2-color overprinting (secondary color), 3-color overprinting, or 4-color overprinting (a white ink base) is carried out employing ink-jet recording systems.

[0077]

#### <<Ink Ejection Conditions>>

Preferred ink ejection conditions are such that the recording head and the ink are heated to 35 - 100 °C and preferably to 35 - 80 °C to result in stable ejection.

The viscosity of an actinic radiation curable ink varies widely depending on temperature variation. The resulting viscosity variation results in major effects to the liquid droplet size as well as the liquid droplet ejection



rate to degrade image quality. As a result, it is necessary to maintain the raised temperature at a constant value. The controlled temperature range of ink temperature is preferably set temperature  $\pm 5$  °C, more preferably set temperature  $\pm 2$  °C, and still more preferably set temperature  $\pm 1$  °C.

[0078]

Further, in the present invention, the volume of liquid droplets ejected from each nozzle is preferably 2 - 15 pl.

[0079]

Originally, in order to form highly detailed images, it is necessary to maintain the volume of liquid droplets in the aforesaid range. However, when the aforesaid volume of a single liquid droplet is ejected, it becomes more difficult to achieve the aforesaid ejection stability. According to the present invention, even though ejection is carried out at a small droplet volume such as 2 - 15 pl, ejection stability is enhanced, whereby it is possible to consistently form highly detailed images.

[0080]

<<Radiation Exposure Conditions after Ink Impingement>>

In the image recording method employing the actinic radiation curable composition (ink) according to the present

invention, inks are cured while exposed to actinic radiation such as ultraviolet radiation. Examples of radiation sources which are employed for actinic radiation exposure include, but are not limited, to low pressure mercury lamps, UV lasers, xenon flash lamps, insectivorous lamps, black light lamps, insecticide lamps, cold cathode tubes, and LEDs.

[0081]

In the image recording method employing the actinic radiation curable composition (ink) according to the present invention, actinic radiation is preferably applied between 0.001 and 2.0 seconds after ink impingement and more preferably exposed between 0.001 and 1.0 second. In order to form highly detailed images, it is particularly important that exposure timing is as quick as possible.

[0082]

Disclosed as an actinic radiation exposure method is a basic method in Japanese Patent Application Open to Public Inspection No. 60-132767. According to the aforesaid patent, light sources are arranged on both sides of a recording head unit, and the recording head as well as the light sources is scanned employing a shuttle system. Exposure is to be performed for a definite time after ink impingement. Further, curing is completed employing another light source

which is not driven. U.S. Patent No. 6,145,979 discloses a method in which optical fibers are employed as an exposure method and in addition, a method in which UV radiation is exposed to a recording section while a collimated radiation is incident to the mirror surface provided on the side surface of a recording head unit. In the image forming method employing the actinic radiation curable composition (ink) according to the present invention, any of these methods are available.

[0083]

Further, the following method is also one of the preferable embodiments. Actinic radiation exposure is divided into two steps. Initially, while employing the aforesaid method, actinic radiation is exposed between 0.001 - 2.0 seconds after ink impingement. After completing all printing, further actinic radiation is applied. By dividing actinic radiation exposure into two steps, it is possible to minimize contraction of recording materials which occurs during curing of the ink.

[0084]

Heretofore, in the UV ink-jet systems, in order to minimize spreading of ink dots as well as bleeding after ink impingement, it is common to use high illuminance light

sources which result in a total electric power consumption of at least 1 kW·hr. However, it has been impossible to use such light sources especially for printing on shrink labels due to excessively large contraction of recording materials.

[0085]

In the present invention, it is further preferable that the total electric power consumption of the light source used for exposure of actinic radiation is less than 1 kW·hr.

Examples of light sources resulting in the total electric power consumption of less than 1 kW·hr include, but are not limited, to fluorescent tubes, cold cathode tubes and LEDs. The total electric power consumption is the sum of electric power used to drive light sources and emit radiation. Based on the present invention, by employing minimal electric power as above, it is possible to carry out ink-jet recording which results in excellent text quality, minimizes color mixing and makes it possible to very consistently record highly detailed images.

[0086]

<<Printed Matter>>

Printed matter which is prepared by employing the actinic radiation curable composition (ink) will now be described.

[0087]

Printed matter of the present invention is characterized in being prepared by employing the image forming method of the present invention and/or the image forming apparatus described in the present invention, while using non-absorptive recording materials. "Non-absorptive", as described herein, means that the actinic radiation curable composition (ink) is not absorbed. In the present invention, recording materials which have an ink transfer amount of at most  $0.1 \text{ ml/mm}^2$  determined by Bristow's method, described below, or substantially  $0 \text{ ml/mm}^2$  are defined as non-absorptive recording materials.

[0088]

<<Bristow's Method>>

Bristow's method, as described in the present invention, refers to the method which determines liquid absorption behavior of paper and paper board within a short time. In practice, measurement is performed in accordance to J. TAPPI Paper and Pulp Test Method No. 51-87 Test Method of Liquid Absorption of Paper or Paper Board (Bristow's Method). The resulting liquid absorption is represented by ink transfer amount ( $\text{ml/m}^2$ ) within a contact time of 40 milliseconds. Incidentally, in the aforesaid measurement

method, pure water (ion exchanged water) is employed. However, in the present invention, in order to more easily discriminate the measured area, water-soluble dyes may be incorporated in an amount of at most 2 percent.

[0089]

One example of the specific measurement methods will now be described.

The ink transfer amount is measured as follows. A recording medium is allowed to stand at an ambience of 25 °C and 50 percent relative humidity for at least 12 hours. Thereafter, measurement is carried out employing, for example, Bristow Tester Type II (a pressing system), manufactured by Kumagai Riki Kogyo Co., Ltd., which is a dynamic liquid absorbability testing device. In order to enhance measurement accuracy, a commercially available water based ink-jet ink (e.g., magenta ink) is employed as the liquid used for the measurement. After the specified contact time, it is possible to determine the ink transfer amount by measuring the area dyed with magenta on the recording medium.

[0090]

#### <<Non-absorptive Recording Materials>

As supports for the present invention, various types of non-absorptive supports can be used other than common coated

paper and non-coated paper. Among them, preferably used are non-absorptive plastics and film supports used for soft packaging materials.

Examples of non-absorptive supports are various types of plastic films including PET (polyethylene terephthalate) film, OPS (oriented polystyrene) film, OPP (oriented polypropylene) film, ONy (oriented nylon) film, PVC (polyvinyl chloride) film, PE film, and TAC film. Employed as other plastic films may be polycarbonate, acrylic resins, ABS, acetal, PVA, and rubber. Further, metal and glass may also be employed.

Of these recording materials, when images are formed specifically on PET film, OPS film, OPP film, ONy film, or PVC film which are thermally shrinkable, the effects of the present invention are more pronounced. These substrates tend to curl and deform due to contraction during ink curing and heat generated during the curing reaction. In addition, it is difficult for the ink layer to keep up with contraction of the aforesaid substrate.

[0091]

The surface energy values of the aforementioned plastic films different from each other. It has been a problem that a dot diameter after ink-jetting varies depending on the

recording materials. The preferred composition of the present invention includes OPP film and OPS film having a low surface energy and PET film having a relatively large surface energy. A wide variety of recording materials having a wettability index of 0.035 to 0.06 J/m<sup>2</sup> can be used to yield a detailed image. Preferred recording materials for the present invention are those having a wettability index of 0.040 to 0.06 J/m<sup>2</sup>.

[0092]

In the present invention, from the viewpoint of the cost of recording materials such as packaging cost as well as production cost, print production efficiency, and compatibility with prints of various sizes, it is more advantageous to use long (web) recording materials.

[0093]

#### [EXAMPLES]

The present invention will now be described with reference to examples. However, the present invention is not limited thereto.

[0094]

Example

(Preparation of Coating Compositions)



Each of the actinic radiation curable compositions (inks) was prepared in such a manner that each of Present Invention Compounds 1, 2, 3, and 8, and Comparative Compound, being a cationically polymerizable compound, shown in Table 1, and a compound (SP-152, manufactured by Asahi Denka Co., Ltd.) were dissolved while stirring and the resulting solutions were mixed.

Table 1

	Example 1	Example 2	Example 3	Example 4	Comparative Example
Compound Example 1 2-trifluoromethylcarbonyl-3,3- dimethyloxetane	95%	-	-	-	-
Compound Example 2 2-methoxy-3,3-dimethyloxetane	-	95%	-	-	-
Compound Example 3 3,3'-trimethylenebis(3-ethyloxetane)	-	-	95%	-	-
Compound Example 8 2,2'-trimethylenebis(3,4,4- trimethyloxetane)	-	-	-	95%	-
Comparative Compound 1 1'-bis[3-ethyloxetane-3-yl]methyl ether	-	-	-	-	95%
SP-152 (manufactured by Asahi Denka Co., Ltd.)	5%	5%	5%	5%	5%

[0096]

The aforesaid compositions were well stirred and dissolved. Thereafter, the resulting ink was applied onto a 38  $\mu\text{m}$  thick PET (polyethylene terephthalate) support, employing a #8 wire bar, whereby a coated layer was prepared. The resulting coated layer was evaluated employing the method described below.

[0097]

<Evaluation>

The resulting coated layer was exposed employing a 4 kW high pressure mercury lamp unit having a substrate conveyer. Subsequently curing rate was determined.

[0098]

Illuminance onto the exposed surface was set at 1,000  $\text{mW}/\text{cm}^2$ , and energy of the exposed radiation was controlled by varying the speed of the aforesaid conveyer. The radiation was exposed to the entire ink coated surface while the integral radiation amount was variable from 50 to 600  $\text{mJ}/\text{cm}^2$ . Curing speed was determined when no surface tackiness was noticed. The aforesaid curing speed was evaluated at 25 °C and 30 percent relative humidity.

[0099]

Further, each of the prepared inks was stored at 55 °C and the resulting viscosity was determined at 25 °C (employing a Type E Viscosimeter, manufactured by Tokyo Keiki Co.).

Table 2

		Electron Density of Oxetane Oxygen	Electron Density of Oxygen out of Oxetane	35% RH Speed mJ/cm <sup>2</sup>	Viscosity before Storage	Viscosity after 7- Day Storage at 55 °C
Example 1	2- trifluoromethylcarbonyl -3,3-dimethyloxetane	-0.245	-0.182	80	30m·Pa	30m·Pa
Example 2	2-methoxy-3,3- dimethyloxetane	-0.301	-0.28	90	35m·Pa	35m·Pa
Example 3	3,3'-trimethylenebis(3- ethyloxetane)	-0.281	-	80	35m·Pa	35m·Pa
Example 4	2,2'- trimethylenebis(3,4,4- trimethyloxetane)	-0.277	-	50	35m·Pa	35m·Pa
Comparative Example	1,1'-bis[3- ethyloxetane-3- yl]methyl ether	-0.27	-0.27	110	20m·Pa	Gel formation

[0101]

As can clearly be seen from Table 2, actinic radiation curable compositions (inks) according to the present invention exhibited high speed as well as excellent storage stability to the degree that inks according to the present invention resulted in a minimal increase in viscosity, while the ink of Comparative Example, in which the conventional oxetane compound was used, gelled.

[0102]

[EFFECTS OF THE INVENTION]

Actinic radiation curable ink compositions usable in ink can be prepared which exhibit excellent curability as well as excellent storage stability.

[NAME OF DOCUMENT] ABSTRACT

[SUMMARY]

[THE PROBLEMS TO BE SOLVED]

an objective of the present invention is to provide a composition which exhibits excellent curability, excellent storage stability in the form of an actinic radiation curable composition, minimal variation of physical properties due to an increase in viscosity when stored in the form of a composition, high speed, and excellent storage stability.

[MEANS TO SOLVE THE PROBLEMS]

An actinic radiation curable composition comprising (a) an oxetane compound in which an oxygen atom, which constitutes at least one oxetane ring in a compound which has at least two oxetane ring structures in the molecule, exhibits the highest electron density of all atoms constituting the molecule, and (b) a compound which generates a cation when exposed to actinic radiation.

[SELECTED DRAWINGS]      None